

**National Aeronautics and Space Administration
Graduate Student Research Program Proposal
Academic Year 1997-8**

The design and development of a regenerative separatory column using calixarenes as a polymeric backbone for the purification of water from urine.

Introduction

The objective of this research project is to design calixarenes, cup-shaped molecules, with the specific binding sites to the sodium chloride and nitrogen containing components of urine, such as urea and uric acid, in urine. The following partition of the research accomplishes this objective:

- Functionalization of calixarene
- Development of a calixarene based media for the separatory process
- Design of the column regeneration protocol.

Research Progress

In efforts to design a calixarene molecule with specific binding to nitrogen containing components of urine, functionalization of the upper rim of the calixarene was investigated. The calixarene proposed to capture the alkali salt is an ionophoric calix[4]arene with a bianthracene moiety attachment. These functionalized calixarenes increase the depth of the cavity and introduce spectroscopic properties to the system. Not only does this molecule possess the ability to capture the alkali metal, it serves as a chromophoric switch. This chromophoric switch is activate/deactivated by varying wavelengths of light. This chromophoric calixarene provides a molecular detection for the visual color change of host-guest complexing. Spectroscopic instrumentation detects a color change. The direction of this research involves the incorporation of calixarenes into a polymeric backbone. The upper rim of the calixarene incorporated into a polymeric backbone provides stability for the calixarene in a separatory system.

Molecular separations, via the use of synthetic membranes, are beginning to yield new and more energy-efficient methods for chemical processing. The development of the design and control of pore structure at the molecular level is in the beginning stages. The creation of novel materials that exhibit high permeation selectivity and high permeation rates are not only valuable but necessary. Porous surfactants, derived from calixarenes, synthesize a perforated monolayer--a two-dimensional network of molecular pores. The porosity of the membrane is determination by the size of the calixarene cavity. These perforated membranes serve as a basis for fabricating thin film composite membrane bearing uniform, oriented, and adjustable micropores.

The construction of composite membranes that distinguish permeants on the basis of their molecular size is the research topic for Regen et al.¹² His research calls for the functionalization of the bottom rim of the calixarene with aliphatic chains and mercurating

the upper rim of the calixarene to achieve a perforated monolayer. This mercurization would allow the calixarene to form a monolayer on the water surface on a Langmuir-Blodgett trough. The calixarene would lie at the air-water interface in a hexagonally packed array and all of the mercury ions are in contact with the water. The compressed monolayer is transferred to glass microscope slide once the monolayer is achieved. Although this method has its advantages, there remains areas of improvements. Due to the hazards that mercury poses on the environment, a less toxic procedure is necessary. The Langmuir-Blodgett technique require mechanical forces to create and maintain the monolayer. A chemically synthesized membrane would not depend on mechanical forces to maintain shape nor its porosity.

The United State Patent 4,306,073 copyrights the synthesis of calixarenes with siloxane polymeric backbone.¹³ However, various papers have suggested that the calixarene does not retain its cup shape once the calixarene is incorporate into the siloxane backbone. Unfortunately, the procedure described in patent 4,306,073 produced low yields of impure product.

The low yield derived from following patent 4,306,073 and the limitations of working on the Langmuir-Blodgett dictate the change in research methodology. The research will no longer focus on incorporating the chromophoric calixarene onto a siloxane backbone. The new direction of this research will focus on the incorporation of the calixarene molecule directly into the polymer chain. The free radical polymerization of calixarene with 2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS) to produce a water-soluble polymer membrane.¹¹

Educational Advancements

I successfully completed the academic requirements for a Master of Science in Chemistry from Georgia Institute of Technology. I was accepted in the doctoral program in the department of Textiles and Fiber Engineering. The discipline of Textiles and Fiber Engineering affords me the opportunity to utilize my diverse educational background. This department has the research and technology that can facilitate a more productive working and learning environment.

REFERENCES

1. Shinkai, S.; Linnane, P. *Chem. & Ind.* 1994, 811.
2. Macomber, R. *J. Chem. Ed.* 1992, 69, 375.
3. Diederich, F. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 362.
4. Shinkai, S.; Manabe, O.; Araki, K. *J. Am. Chem. Soc.* 1988, 110, 7214.
5. Nomura, E.; Taniguchi, H.; Tamura, S. *Chem. Let.*, 1989, 1125.
6. Shinkai, S.; Araki, K.; Shitbata, J.; Tsugawa, D.; Manabe, O. *J. Chem. Soc., Perkin Trans. 1.* 1990, 3333.
7. Coleman, A.; Bott, S.; Atwood, J.L. *Include. Phenom.* 1986, 5, 581.
8. Sheridan, R.; Whitlock, H. W. *J. Amer. Chem. Soc.* 1986, 108, 7120.
9. De Boer, J.; Reinhoudt, D. *J. Amer. Chem. Soc.* 1985, 107, 5347.
10. Shinkai, S.; Manabe, O.; Araki, K.; Shitbata, J. *J. Chem. Soc. Perkin Trans. I.* 1989, 195.
11. Guillet, J. E.; Gravett, D. M. *Macromolecules.* 1995, 29, 618.
12. Regen, S. L.; Conner, M.; Janout, V. *J. Am. Chem. Soc.* 1993, 115, 1178.
13. Darnes, R.; Wyler, D. U. S. Patent 362,803. 1980.

Summer Research Assignment

**Langley Research Center: UV & IR Detector Technology Measurements Science
and Instrument Technology Division**

Dr. Billy T. Upchurch

The temperature sensitive paint, TSP, system visually and thermally detects the effects of laminar and turbulent flow over the body of the aircraft. The temperature sensitive paint is actually a system of a top coat and primer coat of paint against the material of the aircraft. The top coat of paints possesses a lumiphore and a polymer binder. The lumiphore will denote a color change when there is a temperature change. The polymer binder in the top coat will hold the lumiphore in place without quenching the efficacy of the lumiphore. The primer coat is an insulator that protects the top coat of paint from aircraft surface heat. The insulating paint must have a low thermal conductivity, adhere to the metal surface of the aircraft, adhere to the finish coat, and be able to withstand cryogenic conditions in the wind tunnel.

Project Phase I: Computational Thermal Conductivity Studies

The research project is to design a TSP with insulating properties. An important part of this research project is to discover the thermal conductivity of polymers for TSP. Ingredients classify this paint. Several polymer candidates were investigated to determine their effectiveness in TSP. The thermal conductivity is of great importance in polymers for high thermal insulation. The low thermal conductivities of polymers and of foams coupled with other desirable properties, have made polymers and polymeric foams the insulating materials of choice in many applications.

For a given polymeric structure, the following are the most important factors affecting thermal conductivity: morphology (crystallinity and orientation), formulation (additives, fillers and impurities), humidity (especially for polar polymers), temperature, and pressure. An estimation of the thermal conductivity of the polymer candidates is obtained using Windowchem--a computer program to calculate the thermal conductivity polymers. The Windowchem program calculates thermal conductivity using the molecular weight, polymeric backbone and pendant groups of liquids and gases. Several compounds were tested to validate whether this program was valid for polymeric systems at discrete temperature points and over a range of temperatures.

The data are as follows:

TABLE I: Estimation of the Accuracy of WindowChem's Thermal Conductivity Values

Compound Name	Temperature °C	Est. Thermal Conductivity Cal/(°C m sec)	Actual Thermal Conductivity Cal/(°C m sec)
Chloroform	50	0.0002378	0.0002333
Methylene chloride	0	0.0003014	0.0002908
Triethylamine	44.4	0.0002890	0.0002664
Oleic Acid	26.5	0.0003026	0.0005551

The data in table I proved to be fairly accurate in evaluating the thermal conductivity at a specific temperature. Because of the great sensitivity of the thermal conductivity to crystallinity, orientation and formulation, a wide range of values (measured at the same temperature) exists for polymers in standard tables. It was beneficial to test this program over a large temperature range, because the desired polymer will need to perform over the range of [-150 °C-+60 °C].

TABLE II: Estimation of the Accuracy of WindowChem's Thermal Conductivity Values for Poly (vinyl chloride) over a 270°C Temperature Range

Temperature °C	Actual Thermal Conductivity W m ⁻¹ K ⁻¹	Est. Thermal Conductivity W m ⁻¹ K ⁻¹
-170	0.129	0.2087
-50	0.152	0.1648
0	0.158	0.1443
100	0.165	0.0958

The data from table II proved that the Windowchem program was not accurate in calculating the thermal conductivity over such a wide temperature range. However, over a shorter range of approximately 100°C, calculated data were acceptable. There are several factors that this program does not take into consideration such as:

- The glass transition temperature, T_g,
- The degree of crystallization,
- The amorphous region of the polymer.

Each of these factors plays a vital role in determining the thermal conductivity of the polymer. Thermal conductivity increases greatly with increasing strength of the bonds located in the direction of heat transport. For example, the covalent chemical bonds along a polymer chain backbone are far more effective in transporting heat, than are nonbonded interactions in directions' perpendicular to the back bone.¹

Project Phase II: Mathematical Thermal Conductivity Analysis

There is an approach made by Jozef Bicerano in Prediction of Polymer Properties. This book gives a mathematical formula to calculate the thermal conductivity.¹

$$k(T) = k(T_g) (T/T_g)^{0.22}$$

Amorphous polymers, $T < T_g$

$$k(T) = k(T_g) [1.2 - 0.2(T/T_g)]$$

Amorphous polymers, $T > T_g$

There are actually four different approaches to determining thermal conductivity. Bicerano's approach is the most recent. It combines two approaches and modifies the equation to include some additional parameters not included in the others. Polymer history depends on the morphology, formulations, temperature, and pressure are the most important factors that affect the thermal conductivity.² Therefore, predictive methods for the thermal conductivity are inevitably limited by all of these factors, and they can at best provide rough estimates.